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(54) Title: ONE STEP PROCESS FOR PREPARING A 1,3-DIOL

(57) Abstract: A process for an improved oxirane hydroformylation catalyst, the improved oxirane hydroformylation catalyst, and a one step process for preparing a 1,3-diol in the presence of such a catalyst. One process for preparing the hydroformylation catalyst involves:a) forming a complex (A) by contacting a ruthenium(0) compound with a ditertiary phosphine ligand; and b) forming a complex (B) by subjecting complex (A) to a redox reaction with a cobalt(0) carbonyl compound. The one step hydroformylation process for preparing a 1,3-diol comprises the reaction of an oxirane with syngas at hydroformylation conditions in an inert solvent in the presence of the above hydroformylation catalyst where recovery of product is preferably accomplished via phase separation of a diol rich phase from the bulk reaction liquor.

ONE STEP PROCESS FOR PREPARING A 1,3-DIOL

Field of the Invention

The present invention relates to a one step process for preparing a 1,3-diol, and 1,3-propanediol in particular.

Background of the Invention

5   1,3-Diols have plenty of uses, particularly in the synthesis of polymers. For instance, "CORTERRA" (trademark) is a polyester made of 1,3-propanediol (hereinafter 'PDO') and terephthalic acid, which polymer has outstanding properties. Other 1,3-diols

10   may find similar use. Commercially attractive routes to prepare such 1,3-diols are therefore highly desirable.

US-A-5304691 and the art described therein relates to a process for making PDO and HPA (3-

15   hydroxypropanal, a 3-hydroxyaldehyde). In US-A-5304691, PDO and HPA are made by intimately contacting an oxirane (ethylene oxide, hereinafter 'EO'), a ditertiary phosphine-modified cobalt carbonyl catalyst, a ruthenium catalyst promoter, and

20   syngas (carbon monoxide and hydrogen) in an inert reaction solvent at hydroformylation reaction conditions. A PDO yield of up to 86-87 mole% is reported, using a catalyst comprising cobalt ligated with 1,2-bis(9-phosphabicyclononyl)ethane as

25   bidentate ligand, and either triruthenium(0) dodecarbonyl or bis[ruthenium tricarbonyl dichloride] as cocatalyst.

As mentioned, this process typically results in
the synthesis of a mixture of HPA and PDO. However,
it would be much more attractive to produce PDO in a
single step, or in a higher yield, obviously without

5   co-producing impurities that inhibit the use of PDO
in the preparation of polymers etc. In order for this
process to be particularly successful, recycle of the
catalyst without significant deterioration of
performance is needed. Surprisingly such a process,

10   and a catalyst suitably used therein, has now been
found.

Summary of the Invention

Accordingly the present invention provides a
process for an improved oxirane hydroformylation

15.   catalyst, the improved oxirane hydroformylation
catalyst, and a one step process for preparing a 1,3-
diol in the presence of such a catalyst where
recovery of product is preferably accomplished via
phase separation of a diol rich phase from the bulk

20   reaction liquor.

In accordance with the present invention there is
provided a process for preparing a hydroformylation
catalyst which involves:

a)   forming a complex (A) by contacting a

25   ruthenium(0) compound with a ditertiary phosphine
ligand; and

b)   forming a complex (B) by subjecting complex (A)
to a redox reaction with a cobalt(0) carbonyl
compound.

30   In accordance with the present invention there is
also provided a hydroformylation catalyst prepared by
a process which involves:

a)   forming a complex (A) by contacting a ruthenium (0) compound with a ditertiary phosphine ligand; and

b)   forming a complex (B) by subjecting complex (A) to a redox reaction with a cobalt(0) carbonyl compound.   Said hydroformylation catalyst preferably has a cobalt carbonyl anion IR band at 1890 or 1894 cm^{-1}.

The novel oxirane hydroformylation catalyst involves complex (B), which is postulated to be a ruthenium(+1)-phosphine bidentate : cobalt (-1) complex. The characterizing feature of the novel catalyst is that the metal being ligated is ruthenium, rather than cobalt as in US-A-5304691 referred to above. Indeed, upon analysis of both systems a distinct difference in the catalysts was noted in the IR spectra. The IR spectrum of the catalyst according to the present invention revealed the presence of phosphorus-ruthenium bands at 2107, 2053, and 2040 cm^{-1} , which are not present in the IR spectrum of the catalyst according to the invention of US-A-5304691.

Furthermore, the present invention also provides a one step hydroformylation process for preparing a 1,3-diol, comprising the reaction of an oxirane with syngas at hydroformylation conditions in an inert solvent in the presence of a hydroformylation catalyst prepared by a process which involves:

a)   forming a complex (A) by contacting a ruthenium (0) compound with a ditertiary phosphine ligand; and

b)   forming a complex (B) by subjecting complex (A) to a redox reaction with a cobalt(0) carbonyl compound.

In accordance with the present invention there is
further provided a one step hydroformylation process
for preparing a 1,3-diol, comprising the reaction of
an oxirane with syngas at hydroformylation conditions
in an inert solvent in the presence of a
hydroformylation catalyst which is a ruthenium (+1)-
phosphine bidentate : cobalt (-1) complex wherein the
ligated metal is ruthenium, under conditions which
preferably upon completion of the oxirane/syngas
reaction cause a phase separation of the reaction
mixture into an upper solvent phase which is rich in
catalyst and a lower phase which is rich in the 1,3-
diol, recycling the upper phase rich in catalyst
directly to the hydroformylation reaction for further
reaction with previously unreacted starting
materials, and recovering the 1,3-diol from the lower
phase rich in 1,3-diol.

In accordance with the present invention there is
still further provided a hydroformylation catalyst
which is a ruthenium (+1)-phosphine bidentate :
cobalt (-1) complex wherein the ligated metal is
ruthenium.

Brief Description of the Figures

The present invention will now be described by
way of example with reference to the accompanying
drawings, in which:

Figure 1 is a comparison of the in-situ IR
spectrum of the invention catalyst (as prepared) with
the in-situ IR spectrum of a comparison catalyst (as
prepared);

Figure 2 is a comparison of the in-situ IR
spectrum of the HPA absorbance at 1728 cm^{-1} over the

course of the reaction using a catalyst in accordance
with the present invention, as compared to the
comparison catalyst; and

Figure 3 is an IR spectrum of catalyst regions of
the isolated solid of Example 5.

Detailed Description of the Present Invention

Oxiranes of up to 10 carbon atoms, preferably up
to 6 carbon atoms, and ethylene oxide in particular
may be converted into their corresponding 1,3-diols
by the hydroformylation reaction with syngas in the
presence of complex (B) as catalyst.

The 1,3-diols are made by charging the oxirane,
catalyst, optional cocatalyst and/or catalyst
promoter and reaction solvent to a pressure reactor
with the introduction of syngas (a mixture of
hydrogen and carbon monoxide, suitably in a molar
ratio of 1:1 to 8:1, preferably 2:1 to 6:1) under
hydroformylation conditions.

The process of the present invention comprises
batch-type processes, continuous processes and mixed
forms thereof.

For best results, the process is conducted under
conditions of elevated temperature and pressure.
Reaction temperatures range from ambient temperature
to 150 °C, preferably from 50 to 125 °C, and most
preferably from 60 to 110 °C. The reaction pressure
(total pressure, or partial pressure if inert gaseous
diluents are used) is desirably in the range from 5
to 15 MPa, preferably from 8 to 10 MPa. In a batch
process, the reaction will generally be complete
within 1.5 to 5 hours. The reaction solvent is
preferably inert, meaning that it is not consumed

during the course of the reaction. Ideal solvents for
the invention process will solubilize the feed and
products during the course of the reaction, but allow
phase separation at reduced temperatures. Suitable

5   solvents are described in US-A-5304691. For instance,
good results may be achieved with ethers, including
cyclic and acyclic ethers, optionally in combination
with an alcohol or aromatic hydrocarbon. Excellent
results have been achieved with methyl tert butyl

10 ether (MTBE) and a mixture of toluene with
chlorobenzene.

The process of the present invention, in respect
of the preferred embodiment on the synthesis of PDO,
can be conveniently described as follows. Separate,

15 combined or staged streams of EO, syngas and catalyst
are charged to a reaction vessel, which can be a
pressure reaction vessel such as a bubble column or a
stirred autoclave, operated batch-wise or in a
continuous manner.

20 The components of the feed streams are contacted
in a suitable reaction solvent in the presence of the
catalyst of the present invention. The EO will
preferably be maintained throughout the reaction in a
concentration not less than 0.2 % by weight,

25 generally within the range of 0.2 to 20 % by weight,
preferably 1 to 10 % by weight, based on the total
weight of the reaction mixture. The process of the
present invention can be carried out in a continuous
mode, whilst maintaining said EO concentration, by

30 for instance staged EO addition.

At the conclusion of the hydroformylation
reaction, the product mixture is recovered by

conventional methods such as selective extraction, fractional distillation, phase separation, decantation and selective crystallization. The unreacted starting materials as well as the catalyst and reaction solvent may be, and preferably are, recycled for further use.

In a preferred manner of running the process, reaction conditions such as oxirane concentration, catalyst concentration, solvent, product concentration and reaction temperature are selected such as to achieve a homogeneous reaction mixture at elevated temperatures and cause a partitioning of the reaction mixture into an upper solvent phase containing much of the catalyst and a lower phase containing most of the 1,3-propanediol upon cooling the mixture. Such a partitioning facilitates isolation and recovery of product, recyle of catalyst and removal of heavy ends from the solvent system. This process is referred to as a phase separation catalyst recycle / product recovery method.

In this process, the reactor contents are allowed to settle or are transferred to a suitable vessel at or near reaction pressure where upon slight or considerable cooling distinct phases may form that are substantially different, being considerably rich in product or in catalyst and solvent. The phase rich in catalyst and solvent is directly recycled for further reaction with feed materials. Product is recovered from the product rich phase by conventional methods.

It is essential that the reaction is run such that product diol maintains concentration levels in

the reaction mix suitable for phase separation. For
example, concentration of 1,3-propanediol can be from
less than 1 to greater than 50 % by weight,
preferably from 1 to 50% by weight, generally from 8

5   to 32 % by weight and preferably from 16 to 20 % by
weight.   Temperature during quiescent settling of
phases can be from just above the freezing point of
the reaction mixture to 150 °C, and very likely
higher, generally from 27 to 97 °C, and preferably

10   from 37 to 47 °C. The EO concentration is maintained
to avoid the formation of light alcohols and
aldehydes that are miscibilizing agents. Oxiranes
will preferably be maintained throughout the reaction
in a concentration not less than 0.2 % by weight,

15   generally within the range of 0.2 to 20 % by weight,
preferably 1 to 10 % by weight, based on the total
weight of the reaction.   The reaction can be run
with a two-phase system.   However, yields and
selectivities are maximized when high concentrations

20   of product are present in a single phase reaction and
subsequent phase separation occurs upon cooling.

      Partitioning of the reaction mixture can be
promoted by the addition of a phase-split inducing
agent. Suitable agents include glycols such as

25   ethylene glycol and linear alkanes such as dodecane.
Such an agent will be added to the reaction mixture
in an amount within the range of 2 to 10 %w,
preferably 4 to 8 %w based on the total reaction
mixture. Alternate methods include addition of 1,3-

30   propanediol into the reaction mixture to bring
product concentration up to the target proportion.
Also, miscibilizing alcohols and agents with similar

polarity such as ethanol, propanol and isopropanol
can be added initially, then removed prior to, and
subsequently inducing the phase separation.

It is essential in the above described process

5   that as catalyst a complex (B) is used. Complex (B)
is believed to comprise a novel class of ruthenium-
modified catalysts. The characterizing feature of
this novel class involves an oxidized ruthenium metal
that is ligated by a tertiary diphosphine ligand,

10   with a cobalt compound as counter ion, that may be
but preferably is not ligated by a phosphorus ligand.

One compound of this complex comprises the
phosphorus ligand. As mentioned, this ligand is a
ditertiary diphosphine of the general formula:

15   RRP-Q-PR'R'

wherein each group R and R' independently or jointly
is a hydrocarbon moiety of up to 30 carbon atoms, and
Q is an organic bridging group of 2 to 4 atoms in
length. Preferably, the group R and R', when

20   monovalent, each independently is an alkyl,
cycloalkyl, bicycloalkyl or aryl group. Each group R
and R^1 preferably independently has up to 20 carbon
atoms, more preferably up to 12 carbon atoms. Alkyl
and/or cycloalkyl groups are preferred. The group Q

25   preferably comprises carbon atoms, which may form
part of a ring system such as a benzene ring or a
cyclohexane ring. More preferably Q is an alkylene
group of 2, 3 or 4 carbon atoms in length, most
preferably of 2 carbon atoms in length. A non-

30   limiting list of illustrative diphosphines of this
class include 1,2-bis(dimethylphosphino)ethane; 1,2-

bis(diethyl-phosphino)ethane; 1,2-
bis(diisobutylphosphino)ethane; 1,2-
bis(dicyclohexylphosphino)ethane; 1,2-bis(2,4,4-
trimethylpentylphosphino)ethane; 1,2-bis(diethyl-
phosphino)propane; 1,3-bis(diethylphosphino)propane;
1-(diethylphosphino)-3-(dibutylphosphino)propane,
1,2-bis(diphenylphosphino)ethane; 1,2-bis(dicyclo-
hexylphosphino)ethane; 1,2-bis(2-pyridyl, phenyl-
phosphanyl)benzene; 1,2-bis(dicyclopenty-
phosphino)ethane; 1,3-bis(2,4,4-trimethylpenty-
phosphino)propane; and 1,2-bis(diphenyl-phosphino)
benzene. These groups R and R' may be substituted
with non-hydrocarbon groups themselves. Both groups R
and/or both groups R' may also be part of a bivalent
group, to form a ring(s) with the phosphorus atom(s),
such as a phosphacycloalkane of from 5 to 8 atoms.
Examples on 5-ring systems (phospholano-based
ligands) include 1,2-bis(phospholano)ethane, 1,2-
bis(2,5-dimethylphospholano)benzene, optically pure
(R,R), (R,S), (S,S) 1,2-bis(2,5-
dimethylphospholano)ethane or its racemic mixture.
The ring itself may be part of a multi ring system.
Examples of such ring systems may be found in the
aforementioned US-A-5304691 and in WO-A-98/42717. In
the former, phosphabicyclononyl groups are described,
and in the latter, adamantyl-like groups and
phosphatrioxatricyclodecyl groups in particular are
described. Diphosphines wherein both groups R and R'
form a ring with the phosphorus atom are preferred.
The most preferred ligands are 1,2-P,P'-bis(9-
phosphabicyclo[3.3.1] and/or [4.2.1]nonyl) ethane

(hereinafter B9PBN-2), its 1,2-P,P'-propane and/or its 1,3-P,P'-propane analogue (hereinafter B9PBN-3).

Ditertiary phosphine ligands are commercially available. Catalysts prepared therefrom are known in the art and their method of preparation are described in detail in US-A-3401204 and US-A-3527818,. The phosphine ligands may also be partially oxidized to phosphine oxides in the manner described in US-A-5304691.

The ratio of ligand to ruthenium atom may vary from 2:1 to 1:2, preferably from 3:2 to 2:3, more preferably from 5:4 to 4:5 and is most preferably about 1:1. It is hypothesized that this results in a tertiary diphospine ruthenium tricarbonyl compound, but it might also be a bis(tertiary diphosphine ruthenium) pentacarbonyl compound. Unligated ruthenium carbonyl is believed to be an inactive species, and the catalyst preparation therefore seeks to ligate each ruthenium atom.

The counter ion, for best results, is believed to be cobalt tetracarbonyl ($[Co(CO)_4]^-$), although the ion in the active catalyst may be a modification thereof. Part of the cobalt compound may be modified with (excess) tertiary diphosphine, e.g., up to 75 mole%, say up to 50 mole%. However, the counter ion is preferably the non-ligated cobalt tetracarbonyl mentioned before. Cobalt carbonyls can be generated by reaction of a starting cobalt source such as cobalt hydroxide with syngas, as described in J. Falbe, "Carbon Monoxide in Organic Synthesis", Springer-Verlag, NY (1970), or otherwise.

The oxidation state of the ruthenium atom is not
entirely certain (in theory, ruthenium may have a
valence of 0 to 8), which may even change during the
course of the hydroformylation reaction. Accordingly,

5   the molar ratio of ruthenium to cobalt may vary
within relatively broad ranges. Sufficient cobalt
(0) should be added to completely oxidize all of the
complexed ruthenium employed. An excess of cobalt
can be added, but is not of particular value.

10   Suitably, the molar ratio varies from 4:1 to 1:4,
preferably from 2:1 to 1:3, more preferably from 1:1
to 1:2.

The catalyst, complex (B), may be made as follows
hereafter. The first step in the catalyst preparation

15   is the synthesis of complex (A). This may be done by
bringing a suitable Ru(0) source, e.g. triruthenium
dodecacarbonyl, in contact with the tertiary
diphosphine. Alternatively, the triruthenium
dodecacarbonyl may be replaced with less expensive

20   ruthenium sources that in-situ form Ru(0), such as
ruthenium(IV) oxide, hydrate.

The conditions at which these compounds are
allowed to form a complex are not critical.
Temperature and pressure may vary within the ranges

25   already mentioned in respect of the hydroformylation
reaction. Syngas may be used as gas cap during the
complex formation. On the other hand, it is
preferable to use a solvent, preferably the solvent
(if any) used in the hydroformylation reaction.

30   Obviously, this solvent should be capable to dissolve
the active catalyst, without affecting its
properties. Suitable solvents include the ethers

described before, and methyl tertiary-butyl ether
(MTBE) in particular.

The complex (A) may for instance be made by
reacting triruthenium dodecacarbonyl with a
stoichiometric amount of a selected ligand in a
solvent at a temperature within the range of 90 to
130 °C, suitably 100 to 110 °C, under a carbon
monoxide atmosphere, for 1 to 3 hours (i.e. until
completion).

Next, the complex (A) is brought in contact with
a suitable cobalt compound, again at the
aforementioned (non critical) conditions. A suitable
cobalt source is dicobalt octacarbonyl, but other
cobalt(0) complexes, preferably with the exception of
phosphine-modified complexes, may be used as well.
For instance, the selected cobalt carbonyl, and
optional promoters, if any, are added to the solution
which is then maintained at the elevated temperature
for a time of 15 to 60 minutes. This process is
referred to as a step-wise preparation method.

Suitable cobalt sources also include salts which
are reduced to the zero valence state by heat-
treatment e.g. in an atmosphere of hydrogen and
carbon monoxide. Examples of such salts comprise, for
instance, cobalt carboxylates such as acetates and
octanoates, which are preferred, as well as cobalt
salts of mineral acids such as chlorides, fluorides,
sulfates and sulfonates. Operable also are mixtures
of these cobalt salts. It is preferred, however, that
when mixtures are used, at least one component of the
mixture be cobalt alkanoate of 6 to 12 carbon atoms.
The reduction may be performed prior to the use of

the catalysts or it may be accomplished simultaneously with the hydroformylation process in the hydroformylation zone.

It is also within the scope of the present invention to prepare complex (A) by a self-assembly method, wherein all catalyst components are brought together at the same time, but the conditions and in particular the solvent, are selected such as to favour the formation of a ligated ruthenium species, rather than a ligated cobalt species. The presence of the Ru-ligated species rather than the Co-phosphine species may be confirmed by e.g. IR analysis.

In this respect it is emphasized that in the aforementioned US-A-5304691 it was said that the form of the ruthenium is not critical. Although it is suggested to use ruthenium complexes of phosphines described in this reference, any such use is clearly to prepare tertiary phosphine-complexed cobalt carbonyl catalysts, with consequently the loss of the phosphine-complexed ruthenium starting material.

The optimum ratio of oxirane feed to complex (B) will in part depend upon the particular complex employed. However, molar ratios of oxirane to the cobalt within complex (B) from 2:1 to 10,000:1 are generally satisfactory, with molar ratios of from 50:1 to 500:1 being preferred.

Promoters, such as described in the aforementioned US-A-5304691 may be used. The currently preferred promoters, because of their availability and demonstrated promotion of EO conversion are dimethyldodecylamine and triethylamine.

Commercial operation will require efficient catalyst recovery with multiple cycles of essentially complete recycle of catalyst to the reaction. The preferred catalyst recovery process involves separation of the two liquid phase mixture noted previously and recycle of the bulk solvent phase to the reactor and return therewith of at least 60 to 90 % by weight of the starting catalyst.

The present invention is further illustrated by the following examples.

Table 1. Materials and formulations

Co source	CoOc	Cobalt octoate
	DCO	Dicobalt octacarbonyl
Ru source	TRC	Triruthenium dodecacarbonyl
	BRCC	Bis(ruthenium tricarbonylchloride)
Ligand	B9PBN-2	1,2-P,P'-bis(9-phosphabicyclononyl)ethane
	BDEPE	1,2-bis(diethylphosphino)ethane
	BDIPE	1,2-bis(diiosbutylphosphino)ethane
	BDOPE	1,2-bis(2,4,4-trimethylpentylphosphino)ethane
	BDMPE	(R,R) 1,2-bis(dimethylpholano)ethane
Solvent	MTBE	Methyl-t-butyl ether
	T/CB	5:1 v/v mixture of toluene/chlorobenzene
Oxirane	EO	Ethylene oxide
Promoter	DMDA	Dimethyldodecylamine
	NaAc	Sodium acetate

The IR analysis was conducted with in situ cylindrical internal reflectance reactors of the type described by W.R. Moser, J.E. Cnossen, A.W. Wang, and S. A. Krouse in *Journal of Catalysis*, **1985**, **95**, 21; sold by Spectra-Tech Inc. mated to a Nicolet Magna 550 spectrometer. The spectral region of interest includes both the catalyst bands and aldehyde intermediates in the region of 1500 to 2500 cm^{-1}.

Example 1. preparation of complex (B)

In a dry box the following materials were loaded into a 50 ml stainless steel reactor fitted with optics for in-situ reaction monitoring by mid IR analysis: 61 mg TRC (0.286 mmoles Ru), 171 mg B9PBN-2 (0.551 mmoles) and 17 ml of MTBE.

The reactor was sealed, removed from the dry box, placed into the optical bench of an IR spectrometer, and pressurized to 2.2 MPa with carbon monoxide. The reactor was heated to 105 °C and the progress of the complex (A) formation was monitored by IR. Once the temperature reached 105 °C, hydrogen was added to bring the gas composition to an approximate 3:1 syngas ratio.

To this mixture was added a solution of 113 mg DCO and 47 mg of DMDA dissolved in 5 ml of MTBE, using excess 1:1 syngas pressure to bring the total reactor pressure to 8.6 MPa. After an additional 35 minutes at 105 °C the reactor was cooled.

Comparative Example A. preparation of a ligated Co catalyst as in US-A-5304691

In a dry box the following materials were loaded into a 50 ml stainless steel reactor fitted with optics for in-situ reaction monitoring by mid IR analysis: 228 mg CoOc (0.66 mmoles Co), 74 mg BRCC (0.289 mmoles Ru), 222 mg B9PBN-2 (0.715 mmoles), 18 mg sodium acetate (0.22 mmoles) and 23 ml T/CB.

The reactor was sealed, removed from the dry box, placed into the optical bench of an IR spectrometer, and pressurized to 9.0 MPa with 4:1 syngas. The reactor was heated to 130 °C and the progress of the catalyst formation was monitored by IR.

Example 2. preparation of complex (B) by self-assembly

To a 100 ml autoclave was charged in a manner similar to Comparative Example A: 228 mg CoOc (0.66 mmole); 23 ml MTBE; 62 mg TRC (0.29 mmole); 167 mg B9PBN-2 (0.50 mmole); and 17 mg NaAc (0.21 mmole). Again the progress of the catalyst formation was monitored by IR.

Catalyst analysis by IR

Upon addition of B9PBN-2 to TRC, the TRC bands at 2059, 2029 and 2009 cm^{-1} disappeared and an increase was noticed in bands at 1954, 1884 and 1853 cm^{-1}. Upon addition of cobalt carbonyl the oxidation of chelated ruthenium took place accompanied by an instantaneous shift in the IR bands, generating characteristic bands at 2040, 2053, and 2107 cm^{-1} as well as a band at 1890 cm^{-1} that is characteristic for the (unligated) cobalt carbonyl anion.

Referring to Figure 1, the solid line is an in-situ IR spectrum of the complex (B) prepared as described in Example 1. The predominant catalysts bands (at 2040, 2053, and 2107 cm^{-1}) are characteristic of phosphine-modified ruthenium compounds. The dotted line is an in-situ IR spectrum of the comparative catalyst. The in-situ IR spectrum of the complex (B) prepared by the self-assembly method closely corresponded to that of the catalyst made in Example 1.

Example 3. preparation of PDO

At 80 °C 1.1 g EO was added to the reaction mixture of Example 1, using excess 1:1 syngas

pressure. Syngas (1:1) was added as needed to the
reaction mixture to maintain the reaction pressure
between 10.4 and 11.1 MPa. The EO was allowed to
react completely. When cooled, the reactor was opened

5   and a two-phase liquid was isolated. GC analysis
revealed the primary EO-derived product in both
phases was PDO. (Yield of greater than 50 mole%) In a
similar manner, the catalyst of comparative example A
was used. However, the two-phase liquid isolated at

10   the end of this experiment was found to comprise a
lower phase showing an approximately 50/50 mixture of
PDO and HPA and an upper phase containing PDO, HPA
and other materials. (Yield of greater then 50 mole%)

The progress of both reactions were tracked by

15   IR, observing the intensity of absorbance of the
intermediate 3-hydroxypropionaldehyde carbonyl band
(1728 cm^{-1}). The results are reproduced Figure 2.

Using the catalyst of the present invention, the
aldehyde band was seen to rise only slightly at the

20   onset of reaction and then decrease rapidly as the
HPA was converted into PDO. Said band increased
steadily over the course of the reaction when the
catalyst of Comparative Example A was used. This
indicates the superior hydrogenating ability of the

25   catalyst of the present invention.

Comparative Example B

The experiment of Example 3, using the catalyst
of Comparative Example A was essentially followed,
with staged addition of EO (4 steps). In about 4 to 6

30   hours 1,3-PDO was prepared in a yield of 66 mole% at
80 % selectivity. Next, the crude liquid product was
fractionally distilled under vacuum (< 0.1 kPa) to

recover PDO as distillate product fraction. The
remainder was recycled with additional EO and syngas,
plus make-up solvent for a second run. The PDO yield
was found to be only 44 mole%, with only 67 %
5   selectivity. When the remainder of this product was
recycled and allowed to catalyze a third run, the PDO
yield had essentially vanished (2 mole%)

Example 4

The experiment of Example 3, using a catalyst
10   corresponding to that of Example 1, however using
BDEPE instead was essentially followed, with staged
addition of EO (4 steps). In about 4 to 6 hours PDO
was prepared in a yield of 48 mole% at 57 %
selectivity. Next, the crude liquid product was
15   fractionally distilled under vacuum (< 0.1 kPa) to
recover PDO as distillate product fraction. The
remainder was recycled with additional EO and syngas,
plus make-up solvent for a second run. The PDO yield
was found to be 40 mole%, with 54 % selectivity. When
20   the catalyst was recycled and allowed to catalyze the
reaction in this manner for the tenth time, the PDO
yield was still found to be 49 mole%, with 59 %
selectivity.

No apparent loss of catalyst activity was noticed
25   over 12 EO additions. Furthermore, P-NMR of the final
product solution indicated no free BDEPE, with most
of the P-ligand still bound to the ruthenium. It may
therefore be concluded that the novel catalysts of
the present invention possess increased stability.

30   Example 5

Various (scouting) experiments similar to that of
Example 3 were conducted, using a catalyst prepared

by self assembly with an initial Co:Ru:ligand molar
ratio of 2:1:2. The test results are described in the
following Table.

Table 2

Ligand	PDO Yield (mole%)	PDO Selectivity (%)
BDEPE	48-73	83-87
BDIPE	36-53	80-86
BDOPE	31	69
BDMPE	51-71	78-95

From these results it may be concluded that the
catalysts of the present invention are invariably
suitable for the one-step conversion of oxiranes.

Example 6, preparation of complex (B)

In a dry box the following materials were loaded
into a 50 ml stainless steel reactor fitted with zinc
sulfide optics for in-situ reaction monitoring by mid
IR analysis: 128 mg TRC (0.600 mmoles Ru), 186 mg
B9PBN-2 (0.600 mmoles), 9 ml of toluene and 9 ml of
MTBE.

The reactor was sealed, removed from the dry box,
placed into the optical bench of an IR spectrometer,
and pressurized to 1.7 MPa with carbon monoxide. The
reactor was heated to 105 °C and the progress of the
complex (A) formation was monitored by IR. Upon
heating the TRC bands at 2059, 2029 and 2009 cm^{-1}
disappeared and an increase was noticed in bands at
1954, 1882 and 1861 cm^{-1}. After one hour at 105 °C,
hydrogen was added to bring the gas composition to an
approximate 3:1 syngas ratio, 8.29 MPa, and a
solution of 105 mg DCO (0.614 mmoles Co) dissolved in

6 ml of MTBE was added via excess syn gas pressure,
bringing the total reactor pressure to 10.3 MPa.
Upon addition of cobalt carbonyl, the oxidation of
chelated ruthenium took place accompanied by an
instantaneous shift in the IR bands, generating
characteristic bands at 2040, 2053, and 2107 cm^{-1} as
well as a band at 1890 cm^{-1} that is characteristic
for the (unligated) cobalt carbonyl anion. This was
held at 105°C for 1.5 hours without apparent change
in the catalyst composition. Upon heating to 130°C,
the mid IR spectrum indicated no alteration in the
catalyst composition. The reactor was cooled to room
temperature, opened and 0.25 grams of yellow-orange
catalyst solids were isolated by suction filtration
and dried in vacuo. An infrared spectrum of the
isolated solid is shown in Figure 3; the only metal
carbonyl bands present are due to phosphine ligated
ruthenium (I) with a cobalt (-I) tetracarbonyl anion.
No other cobalt carbonyls are present. This complex
is identical to catalyst solids isolated from a one
step 1,3-propanediol reaction of the present
invention.

Example 7. use of isolated complex (B) for
preparation of 1,3-propanediol in a single step.

In a dry box 0.24 grams of catalyst solids from
Example 5 and 23 ml of MTBE were loaded into a 50 ml
stainless steel reactor fitted with zinc sulfide
optics for in-situ reaction monitoring by mid IR
analysis. The reactor was sealed, removed from the
dry box, placed into the optical bench of an IR
spectrometer, and pressurized to 7.0 MPa with 4:1;
hydrogen:carbon monoxide. The reactor was heated to

90°C and 1.9 grams of EO was added to the reaction
mixture using excess 1:1 synthesis gas pressure. The
1:1 synthesis gas was added to the reaction mixture
to maintain a reactor pressure between 10.1 and 10.8
5   MPa. Within an hour the first aliquot of ethylene
oxide was consumed and a second 1.9 grams (3.8 grams
total) of ethylene oxide was injected into the
reactor. The reaction mixture again rapidly consumed
synthesis gas, make up gas being added as needed.
10   The reaction was run to essentially complete EO
consumption during the entire reaction, the IR
spectrum of the catalyst region remains the same as
the starting catalyst solids. Upon cooling and
opening the reactor a two phase mixture was obtained.
15   GC analysis of both phases revealed a PDO yield in
excess of 50% with only trace amounts of HPA
detected.

Example 8, Phase separation catalyst recycle /
product recovery process with catalyst formed by self
20   assembly.

In an inert atmosphere drybox, to a 300 ml
autoclave, 1.85 grams (5.35 mmole Co) cobalt(II)
ethylhexanoate, 1.392 grams (4.48 mmole) 1,2-bis(9-
phosphacyclononyl) ethane, 0.509 grams (2.3 mmole Ru)
25   triruthenium dodecylcarbonyl, 145.85 grams methyl-
tert-butyl ether (MTBE) and 0.30 grams
dimethyldodecyl amine was added. The autoclave body
was sealed and fitted to a benchscale process unit.
Under a headspace of 4:1 H_2 : CO ratio syngas at
30   10.34 MPa g (1500 psig) the mixture was allowed to
reach equilibrium and preform catalyst over 2 hours
at 130 °C   Reactor temperature was reduced to 90 °C.

An addition of 16.96 grams of ethylene oxide (EO) was made and allowed to react with syngas feed at a 2:1 H_2 :CO ratio until the EO is substantially but not completely consumed. The reactor content was

5   transferred under reaction conditions to a phase separation vessel where phase separation began immediately. From the vessel, 12.94 grams lower layer material was isolated. The upper layer reaction liquor was recycled back to the reactor.

10   Compositions of the upper and lower layer are given in Table 3. Catalyst partition data is shown in Table 4. The product, 1,3-propanediol, was produced at an average rate of 20 g/L/hr.

Example 9. Phase separation process, recycle 1

15   The recycled reaction liquor from example 8 was heated to 90°C. An addition of 14.74 grams ethylene oxide was made and allowed to react under a head space of 2:1 H_2 : CO ratio syngas at 10.34 MPa g (1500 psig) until the EO was substantially consumed. The

20   reactor contents were transferred under syngas pressure to a phase separation vessel where phase separation began immediately resulting in the isolation of 8.22 grams of lower layer material. Upper layer reaction liquor was recycled back to the

25   reactor. Compositions of the upper and lower layer are given in Table 3. Catalyst partition data is shown in Table 4. The averaged reaction rate through this recycle gave 14 g/L/hr.

Example 10. Phase separation process, recycle 2

30   The recycled reaction liquor from example 9 was heated to 90 °C. An addition of 14.74 grams ethylene

oxide was made and allowed to react under a head
space of 2:1 H_2 : CO ratio syngas at 10.34 MPa g (1500
psig). The reactor contents were transferred under
syngas pressure to a phase separation vessel where
phase separation began immediately and 8.50 grams of
lower layer material was isolated. Upper layer
reaction liquor was recycled back to the reactor.
Compositions of the upper and lower layer are given
in Table 3. Catalyst partition data is shown in Table
4. The averaged reaction rate through this recycle
gave 37 g/L/hr.

Example 11. Phase separation process, recycle 3

The recycled reaction liquor from example 10 was
heated to 90 °C. An addition of 14.74 grams ethylene
oxide was made and allowed to react under a head
space of 2:1 H_2 : CO ratio syngas at 10.34 MPa g (1500
psig). The reactor contents were transferred under
syngas pressure to a phase separation vessel where
phase separation began immediately and 19.50 grams of
lower layer material was isolated. Upper layer
reaction liquor was recycled back to the reactor.
Compositions of the upper and lower layer are given
in Table 3. Catalyst partition data is shown in Table
4. The averaged reaction rate through this recycle
gave 49 g/L/hr.

Example 12. Phase separation process, recycle 4

The recycled reaction liquor from example 11 was
heated to 90 °C. An addition of 14.74 grams ethylene
oxide was made and allowed to react under a head
space of 2:1 H_2 : CO ratio syngas at 10.34 MPa g
(1500 psig). The reactor contents were transferred

under syngas pressure to a phase separation vessel
where separation began immediately and 32.80 grams of
lower layer material was isolated. Upper layer
reaction liquor was recycled back to the reactor.
Compositions of the upper and lower layer are given
in Table 3. Catalyst partition data is shown in Table
4. The averaged reaction rate through this recycle
gave 34 g/L/hr.

Example 13, Phase separation process, recycle 5

The recycled reaction liquor from example 12 was
heated to 90 °C. An addition of 14.74 grams ethylene
oxide was made and allowed to react under a head
space of 2:1 H_2 : CO ratio syngas at 10.34 MPa g
(1500 psig). The reactor contents were transferred
under syngas pressure to a phase separation vessel
where phase separation began immediately and 71.90
grams of lower layer material was isolated. Upper
layer reaction liquor was recycled back to the
reactor. Compositions of the upper and lower layer
are given in Table 3. Catalyst partition data is
shown in Table 4. The averaged reaction rate through
this recycle gave 30 g/L/hr.

The three most important results for the phase
separation are: 1) achieve an acceptable high enough
rate of production of PDO, 2) recycle most of the
catalyst (in the upper phase), and 3) recover
concentrated product (PDO) in the lower phase.

The data on rate of production of PDO in the
Examples above shows that an acceptable rate of
reaction is achieved and that the catalyst is active
after 5 recycles (#1).

Table 4 shows that a high percentage of the catalyst is directly recycled in the upper phase (#2).

Table 3 shows high recovery of PDO in the lower phase (#3).

Table 3

Phase Split Priimary Compositions				
Example	Layer	PDO %W	MTBE %w	Mass (g)
8	Lower	59.70	18.13	12.94
9	Lower	47.97	16.60	8.22
10	Lower	45.97	19.15	8.50
11	Lower	47.32	21.73	19.50
12	Lower	45.16	20.99	32.80
13	Lower	47.50	25.78	71.90
8	Upper	4.74	85.70	152.36
9	Upper	5.15	87.16	160.04
10	Upper	17.67	77.60	167.19
11	Upper	27.31	54.86	163.47
12	Upper	14.41	69.85	147.04
13	Upper	10.59	80.36	93.46

Table 4

Record / Recycle#	Layer	Ru %w	Co %w	P %w	% Co Catalyst
23661-187-2 / R0	Lower	0.21	0.25	0.23	
23661-188-1 /R1	Lower	0.21	0.18	0.21	91
23661-188-4 / R2	Lower	0.16	0.15	0.14	93
23661-188-7 / R3	Lower	0.14	0.13	0.12	82
23661-188-10 / R4	Lower	0.09	0.1	0.08	78
23661-191-3 / R5	Lower	0.06	0.09	0.04	
23661-187-3 / R0	Upper				
23661-188-2 / R1	Upper	0.08	0.11	0.11	9
23661-188-5 / R2	Upper	0.08	0.1	0.1	7
23661-188-8 / R3	Upper	0.05	0.07	0.06	18
23661-188-11 / R4	Upper	0.05	0.08	0.07	21
23661-191-4 / R5	Upper	0.14	0.11	0.12	

Example 14. Phase separation catalyst recycle /
product recovery process with catalyst prepared via
stepwise procedure

    In an inert atmosphere drybox, to a 300 ml

5   autoclave, 2.14 grams (6.90 mmole) 1,2-bis(9-
phosphacyclononyl) ethane, 0.694 grams (3.25 mmole
Ru) triruthenium dodecylcarbonyl, 119 grams methyl
tert-butyl ether (MTBE) was added. The autoclave body
was sealed and fitted to a benchscale process unit.

10   Under a headspace of 4:1 (H_2 : CO) syngas at 10.34
MPa g (1500 psig) the mixture was allowed to reach
equilibrium over 1 hour at 105C. To the reactor a
solution of, 1.11 grams (6.50 mmole Co) dicobalt
octacarbonyl and 0.108 grams (1.32 mmole) sodium

15   acetate in 33.3 grams MTBE was added at reaction
conditions. The catalyst was allowed to preform at
105°C and 1500 psig for 1.75 hours. Reactor
temperature was reduced to 90°C. Two separate
additions totaling 13.2 grams of ethylene oxide (EO)

20   were made and allowed to react with a 2:1 (H_2 : CO)
syngas feed until substantially all of the EO was
consumed. The reactor contents were transferred under
syngas pressure to a temperature controlled phase
separation vessel. The phase separation was allowed

25   to equilibrate at 43°C. A lower phase of 36.8 grams
was isolated. Upper phase was recycled back to the
reactor. Compositions of the upper and lower phase
are given in Table 5. Catalyst partition data is
shown in Table 6. The product, 1,3-propanediol was

30   produced at an average rate of 26 g/L/hr.

Example 15. Phase separation process, recycle 1

The recycled reaction liquor from example 14 was heated to 90°C. An addition of 14.74 grams ethylene oxide was made and allowed to react under a head space of 2:1 syngas at 10.34 MPa g (1500 psig). The reactor content was transferred under syngas pressure to a phase separation vessel. When equilibrated to 43°C, 28.5 grams of lower phase material was isolated. Upper phase reaction liquor was recycled back to the reactor. Compositions of the upper and lower phase are given in Table 5. Catalyst partition data is shown in Table 6. The averaged reaction rate through this recycle gave 24 g/L/hr.

Example 16. Phase separation process, recycle 2

The recycled reaction liquor from example 15 was heated to 90°C. An addition of 11.00 grams ethylene oxide was made and allowed to react under a head space of 2:1 syngas at 10.34 MPa g (1500 psig). The reactor content was transferred under syngas pressure to a phase separation vessel. When equilibrated to 43° C, 24.8 grams of lower phase material was isolated. Upper phase reaction liquor was recycled back to the reactor. Compositions of the upper and lower phase are given in Table 5. Catalyst partition data is shown in Table 6. The averaged reaction rate through this recycle gave 35 g/L/hr.

Example 17. Phase separation process, recycle 3

The recycled reaction liquor from example 16 was heated to 90°C. An addition of 11.00 grams ethylene oxide was made and allowed to react under a head space of 2:1 syngas at 10.34 MPa (1500 psig). The reactor contents were transferred under syngas

pressure to a phase separation vessel. When
equilibrated to 43°C, 19.1 grams of lower phase
material was isolated. Upper phase reaction liquor
was recycled back to the reactor. Compositions of

5   the upper and lower phase are given in Table 5.
Catalyst partition data is shown in Table 6. The
averaged reaction rate through this recycle gave 23
g/L/hr.

Example 18, Phase separation process, recycle 4

10   The recycled reaction liquor from example 17 was
heated to 90°C. An addition of 11.00 grams ethylene
oxide was made and allowed to react under a head
space of 2:1 syngas at 10.34 MPa (1500 psig). The
reactor content was transferred under syngas pressure

15   to a phase separation vessel. When equilibrated to 43°
C, 38.9 grams of lower phase material was isolated.
Upper phase reaction liquor was recycled back to the
reactor. Compositions of the upper and lower phase
are given in Table 5. Catalyst partition data is

20   shown in Table 6. The averaged reaction rate through
this recycle gave 18 g/L/hr.

Example 19, Phase separation process, recycle 5

The recycled reaction liquor from example 18 was
heated to 90°C. An addition of 11.00 grams ethylene

25   oxide was made and allowed to react under a head
space of 2:1 syngas at 10.34 MPa g (1500 psig). The
reactor content was transferred under syngas pressure
to a phase separation vessel. When equilibrated to
43°C, 38.9 grams of lower phase material was isolated.

30   Upper phase reaction liquor was recycled back to the
reactor. Compositions of the upper and lower phase
are given in Table 5. Catalyst partition data is

shown in Table 6. The averaged reaction rate through this recycle gave 17 g/L/hr.

The data on rate of production of PDO in the examples above shows that an acceptable rate of reaction is achieved and that the catalyst is active after 5 recycles (#1).

Table 6 shows that a high percentage of the catalyst is directly recycled in the upper phase (#2).

Table 5 shows high recovery of PDO in the lower phase (#3).

Table 5

Phase Split Primary Compositions				
Example	Layer	PDO %W	MTBE %w	Mass (g)
14	Lower	63.68	16.15	24.80
15	Lower	49.68	17.39	28.50
16	Lower	68.08	18.03	24.80
17	Lower	53.34	24.31	19.10
18	Lower	33.32	19.39	38.90
19	Lower	30.03	25.91	29.80
14	Upper	7.20	44.63	165.07
15	Upper	8.89	61.35	152.73
16	Upper	36.69	48.66	139.09
17	Upper	16.88	54.86	131.42
18	Upper	6.14	86.65	104.92
19	Upper	27.30	34.57	88.12

Table 6

Record / Recycle#	Layer	Ru %w	Co %w	P %w	% Co Catalyst
23661-187-2 / R0	Lower	0.21	0.25	0.23	
23661-188-1 / R1	Lower	0.21	0.18	0.21	91
23661-188-4 / R2	Lower	0.16	0.15	0.14	93
23661-188-7 / R3	Lower	0.14	0.13	0.12	82
23661-188-10 / R4	Lower	0.09	0.1	0.08	78
23661-191-3 / R5	Lower	0.06	0.09	0.04	
23661-187-3 / R0	Upper				
23661-188-2 / R1	Upper	0.08	0.11	0.11	9
23661-188-5 / R2	Upper	0.08	0.1	0.1	7
23661-188-8 / R3	Upper	0.05	0.07	0.06	18
23661-188-11 / R4	Upper	0.05	0.08	0.07	21
23661-191-4 / R5	Upper	0.14	0.11	0.12	

Example 20. Recycle of lower phase stepwise assembled catalyst

Lower layer samples from examples 14 and 15 rich in 1,3-propanediol product were distilled at 90-110°C under vacuum conditions of 60-4 mm Hg. Collections of methyl tert-butyl ether solvent and 1,3-propanediol were made on the column overhead. Overhead material was greater than 92% 1-3, propanediol. The distillation was carried out such that 75% of the initial charge mass was distilled. A 10 gram sample of the distillation bottoms containing recycled catalyst, some 1-3,propanediol and minor amounts of heavy ends was inventoried into a 300 ml autoclave in an inert atmosphere drybox. To the autoclave was added 74 grams of fresh methyl tert-butyl ether solvent. The autoclave was sealed and fitted to a benchscale process unit. The catalyst liquor was heated to 90°C with stirring. Under a headspace of 4:1 (H_2 :CO) syngas, 11.00 grams of ethylene oxide was added and allowed to react. The reactor contents was transferred under syngas

pressure to a phase separation vessel where at 45°C
phase separation began. When equilibrated, 12.6
grams of lower phase material was isolated. This
lower phase contained 56.47% 1,3-propanediol product.

Upper phase reaction liquor was recycled back to the
reactor and heated to 90°C under a syngas feed
headspace of 2:1 (H_2 : CO). To this recycled solvent
phase, 11.00 grams of ethylene oxide was added and
allowed to react. The reactor contents were
transferred under syngas pressure to a phase
separation vessel where at 43°C phase separation
began. When equilibrated, 24.5 grams of lower phase
material was isolated. This lower phase contained
45.14% 1,3-propanediol product. These reactions
afforded an 81% product yield. This proves that the
catalyst is robust and still active even after being
distilled from the product phase and recycled twice
through the upper phase of subsequent reactions.

Example 21. Use of hexane as phase split inducing
agent

        In an inert atmosphere drybox, to a 300 ml
autoclave, 1.159 grams (3.73 mmole) 1,2-bis(9-
phosphacyclononyl) ethane, 0.696 grams (3.27 mmole
Ru) triruthenium dodecylcarbonyl, 119 grams methyl
tert-butyl ether (MTBE) was added. The autoclave body
was sealed and fitted to a benchscale process unit.
Under a headspace of 4:1 (H_2 :CO) syngas at 10.34 MPa
(1500 psig) the mixture was allowed to reach
equilibrium over 1.5 hour at 105°C. To the reactor a
solution of, 1.13 grams (6.50 mmole Co) dicobalt
octacarbonyl and 0.108 grams (1.32 mmole) sodium
acetate in 33.3 grams MTBE was added at reaction

conditions.   The catalyst was allowed to preform at
105°C and 10.34 MPa g (1500 psig) for 1.75 hours.
Reactor temperature was reduced to 90°C. One addition
of 22 grams of ethylene oxide (EO) was made and

5   allowed to react with a 2:1 (H_2 : CO) syngas feed.
The reactor contents were transferred under syngas
pressure to a temperature controlled phase separation
vessel.   The phase separation was allowed to
equilibrate at 43°C.   A lower phase of 9.746 grams

10   was isolated. Upper phase was recycled back to the
reactor.   As in a fashion similar to above examples
additional ethylene oxide was added to the recycled
upper layer and allowed to react followed by a
temperature induced phase split.   On the third

15   recycle in this example 11.00 grams of ethylene oxide
was added and allowed to react at 90°C and 10.34 MPa g
(1500 psig).   Transfer to phase separation vessel and
subsequent to cooling to 35°C, no phase separation was
apparent.   Two separate additions of 11.00 gram

20   aliquots of ethylene oxide followed by reaction at
stated conditions, and cooling to 33°C did not produce
a 1,3-propanediol concentration where a phase
separation could be made.   We believe that this
reaction produced some by-products, such as ethanol

25   and propanol, that are miscibilizing in nature that
prevented the phase separation.   Addition of 10 grams
of hexane while in the reactor at stated conditions
followed by transfer to the separation vessel and
cooling invoked a phase separation at 77 °C.   This is

30   one way to change the polarity of the system such
that a phase split can be induced.   It is even
possible to add before or during the reaction

miscibilizing agents to ensure a single phase
reaction. These miscibilizing agents can then be
removed, such as by distillation or flashing, to
invoke a phase split for product recovery. After
5   equilibrating to 43°C, the a lower layer sample of
92.7 grams was isolated and contained 48% 1,3-
propanediol product.

<u>C L A I M S</u>

1. A process for preparing a hydroformylation catalyst which involves:

a) forming a complex (A) by contacting a ruthenium (0) compound with a ditertiary phosphine ligand; and

b) forming a complex (B) by subjecting complex (A) to a redox reaction with a cobalt(0) carbonyl compound.

2. The process of claim 1, wherein the ditertiary phosphine ligand is of the general formula:

RRP-Q-PR'R'

wherein each group R and R' independently or jointly is a hydrocarbon moiety of up to 30 carbon atoms, and Q is an organic bridging group of 2 to 4 atoms in length.

3. The process of claim 2, wherein group R and R' each independently is an alkyl, cycloalkyl, bicycloalkyl or aryl group.

4. The process of claim 2 or 3 wherein group Q comprises carbon atoms.

5. The process of claim 4, wherein Q is an alkylene group of 2, 3 or 4 carbon atoms in length.

6. The process of any one of the preceding claims, wherein the ditertiary phosphine ligand is selected from any one or more of 1,2-bis(dicyclohexylphosphino)ethane, 1,2-bis(diphenylphosphino)ethane, 1,2-bis(diethyl-phosphino)ethane, 1-(diethylphosphino)-3-(dibutylphosphino)propane, 1,2-bis(diphenyl-phosphino)benzene, 1,2-bis(dimethylphosphino)ethane,

1,2-bis(2,4,4-trimethylpentylphosphino)ethane, 1,2-
bis(diisobutylphosphino)ethane, 1,2-P,P'-bis(9-
phosphabicyclo[3.3.1] and/or [4.2.1]nonyl)ethane, its
1,2-P,P'-propane, or its 1,3-P,P'-propane analogue.

7.   A hydroformylation catalyst prepared by a process
which involves:

a)   forming a complex (A) by contacting a ruthenium
(0) compound with a ditertiary phosphine ligand; and

b)   forming a complex (B) by subjecting complex (A)
to a redox reaction with a cobalt(0) carbonyl
compound.

8.   A one step hydroformylation process for preparing
a 1,3-diol, comprising the reaction of an oxirane
with syngas at hydroformylation conditions in an
inert solvent in the presence of a hydroformylation
catalyst prepared by a process which involves:

a)   forming a complex (A) by contacting a ruthenium
(0) compound with a ditertiary phosphine ligand; and

b)   forming a complex (B) by subjecting complex (A)
to a redox reaction with a cobalt(0) carbonyl
compound.

9.   A one step hydroformylation process for preparing
a 1,3-diol, comprising the reaction of an oxirane
with syngas at hydroformylation conditions in an
inert solvent in the presence of a hydroformylation
catalyst which is a ruthenium (+1)-phosphine
bidentate : cobalt (-1) complex wherein the ligated
metal is ruthenium, under conditions which preferably
upon completion of the oxirane/syngas reaction cause
a phase separation of the reaction mixture into an
upper solvent phase which is rich in catalyst and a
lower phase which is rich in the 1,3-diol, recycling

the upper phase rich in catalyst directly to the
hydroformylation reaction for further reaction with
previously unreacted starting materials, and
recovering the 1,3-diol from the lower phase rich in

5   1,3-diol.

10. A hydroformylation catalyst which is a ruthenium
(+1)-phosphine bidentate : cobalt (-1) complex
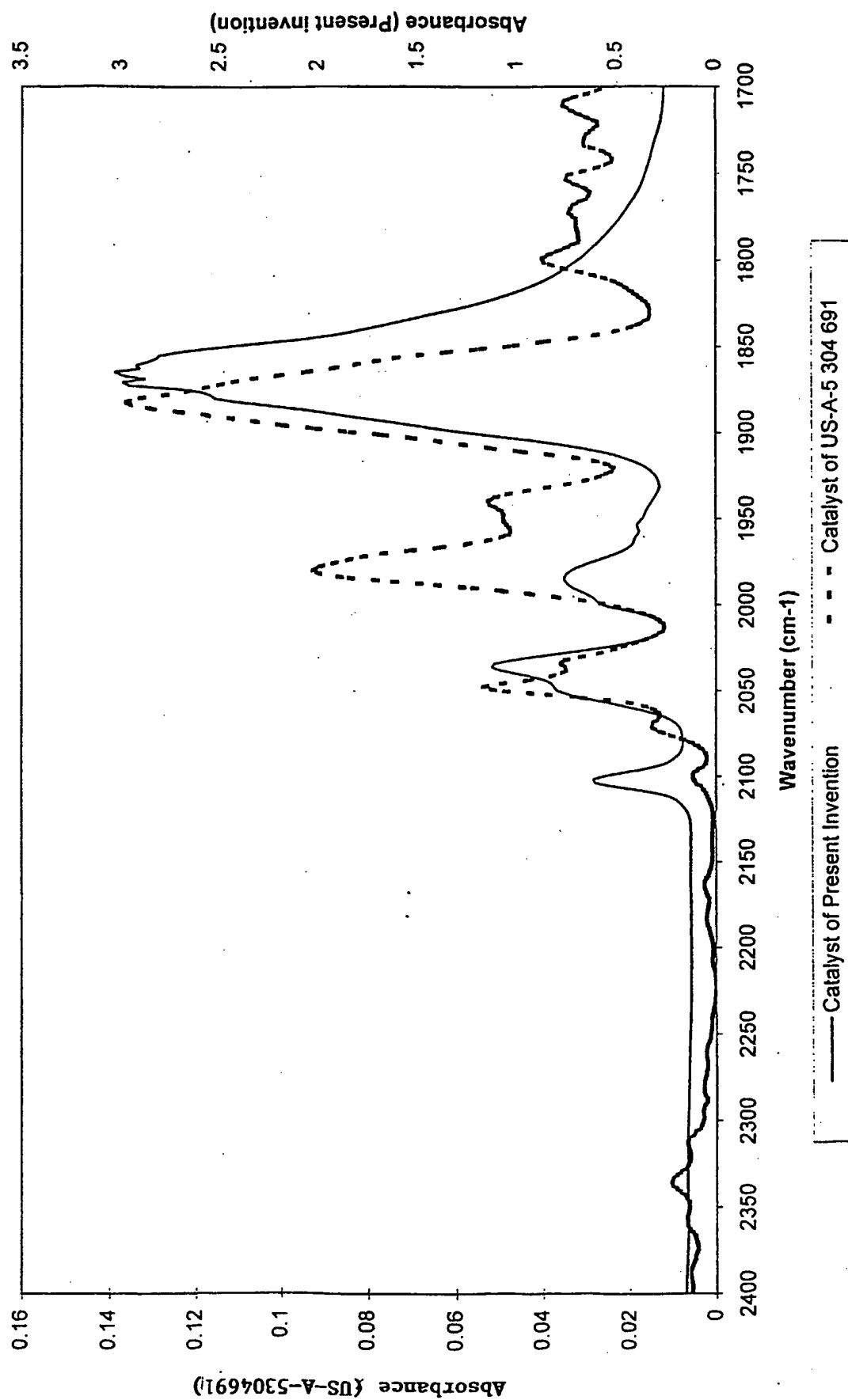wherein the ligated metal is ruthenium.
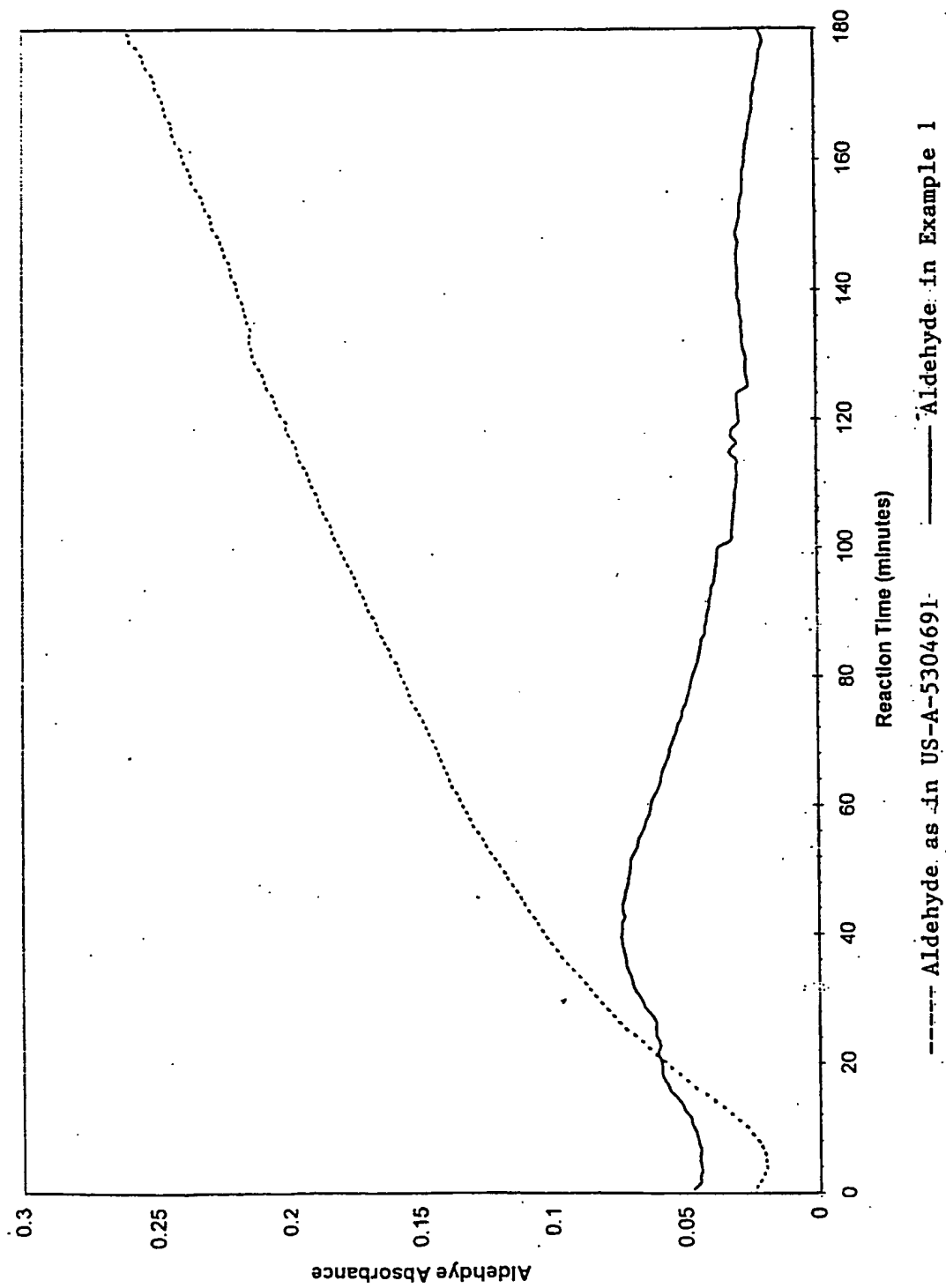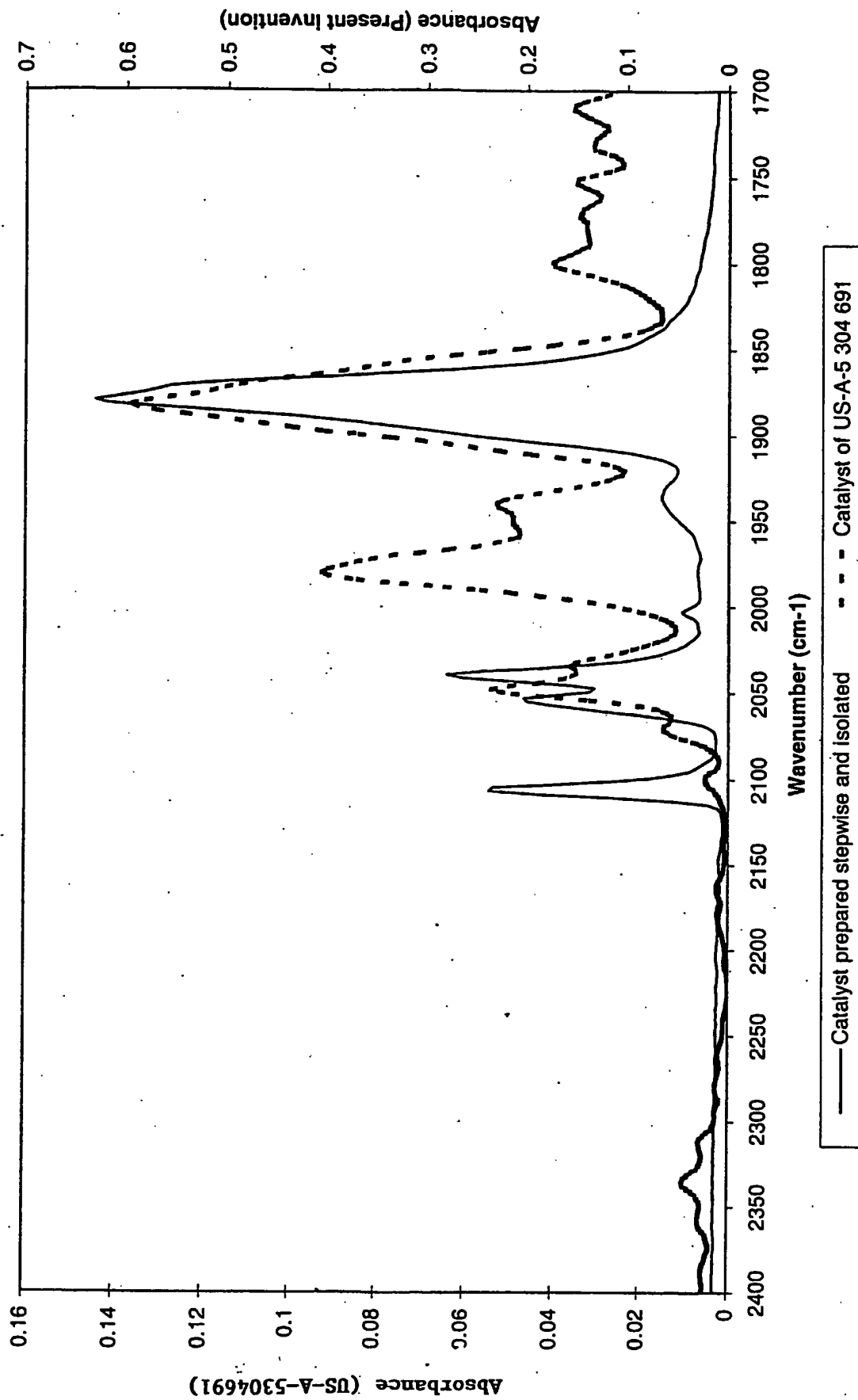
Figure 1

Figure 2

Aldehyde Absorbance

Reaction Time (minutes)

----- Aldehyde as in US-A-5304691 ———— Aldehyde in Example 1

Figure 3

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ONE STEP PROCESS FOR PREPARING A 1,3-DIOL

(57) Abstract: A process for an improved oxirane hydroformylation catalyst, the improved oxirane hydroformylation catalyst, and a one step process for preparing a 1,3-diol in the presence of such a catalyst. One process for preparing the hydroformylation catalyst involves:a) forming a complex (A) by contacting a ruthenium(0) compound with a ditertiary phosphine ligand; and b) forming a complex (B) by subjecting complex (A) to a redox reaction with a cobalt(0) carbonyl compound.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   B01J31/24   B01J31/20   C07C29/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7   B01J   C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 304 691 A (SLAUGH LYNN H ET AL) 19 April 1994 (1994-04-19) column 10, line 55 -column 11, line 10 claims 1-11 column 3, line 25 -column 5, line 9-	1-10
X	US 4 253 987 A (FIATO ROCCO A) 3 March 1981 (1981-03-03) claim 1	1
X	US 4 895 818 A (DUGGAN D MICHAEL ET AL) 23 January 1990 (1990-01-23) column 9, line 36 -column 10, line 38	1

☐ Further documents are listed in the continuation of box C.   ☒ Patent family members are listed in annex.

° Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 October 2001	06/11/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Thion, M

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